

Hydrogen and Halogen Oxide Radical Spectroscopy in the Laboratory and the Atmosphere: Applications to Studies of Stratospheric Ozone Depletion

S. P. Sander^{1,3}, W. J. Bloss¹, R. P. Cagiao¹, L. E. Christensen², R. R. Friedl¹, T. Ingham¹,
F. P. Mills¹, V. Nemtchinov¹ and M. Okumura²

¹Jet Propulsion Laboratory, California Institute of Technology, M/S 183-901
4800 Oak Grove Drive, Pasadena, California, USA 91109

²Department of Chemistry and ³Division of Geological and Planetary Sciences,
California Institute of Technology, Pasadena, California, USA 91125

Research in atmospheric chemistry attempts to understand the complex system of interactions that affect the overall production and loss of the key molecule, ozone. A key element in this process is the measurement of reaction rates and abundances of short-lived species in both laboratory studies and the atmosphere. High resolution spectroscopy plays an important role in both of these endeavors. In this talk we discuss several recent applications from our group's work as applied to species in the hydrogen oxide and halogen oxide radical families.

In the first of these studies, rate coefficients were measured for the recombination reaction, $\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M}$, over the temperature range 210-298 K. Reactions were initiated by laser photolysis at 308 nm and reactants were probed using cw long-path two-color absorption for HO_2 and NO_2 . RF-modulated DFB lasers in a Herriott-cell configuration probed HO_2 radicals in both the $^2\text{A}' \leftarrow ^2\text{A}''$ transition at 1.4 μm as well as the first vibrational overtone in the OH stretch at 1.5 μm .

The kinetics of the formation and destruction of ClOOCl , a key intermediate in the catalytic destruction of ozone in the polar stratosphere, have been studied using both pulsed photolysis and flow tube methods. In the pulsed photolysis experiments, the recombination of ClO radicals has been studied over the temperature range 180-250 K. ClO and ClOOCl were monitored simultaneously using long-path differential absorption between 210-280 nm. The discharge-flow/mass spectrometry method has been used to study the reactions of Cl , Br and NO with ClOOCl using a high-pressure pre-reactor for the *in situ* synthesis of ClOOCl .

Finally, results shall be presented on three years of atmospheric measurements of the OH radical at Table Mountain, California, using a new, compact high-resolution interferometer (FTUVS) which probes several lines in the $\text{A} \leftarrow \text{X}$ progression at 308 nm in solar absorption mode. Applications to the measurement of other trace atmospheric species will be discussed.

This research was carried out by the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration.